# RAW MATERIALS

UDC 666.32/.36

# CRITERIA FOR SELECTING CLAY INITIAL MATERIALS FOR MAKING ALUMINUM SILICATE PROPANTS

**T. V. Vakalova,[1] V. M. Pogrebenkov,[1] and A. A. Reshetova[1]**

Translated from *Steklo i Keramika*, No. 9, pp. 10 – 14, September, 2009.

The possibility of using kaolins from the Ural – Siberian region in the technology of ceramic propants is investigated. The basic criteria for selecting and the physical – chemical principles of using clay initial materials for obtaining high-strength aluminum silicate propants are determined.

***Key words:*** refractory clay initial material, kaolin, mineral composition, sinterability, mullite, aluminum silicate ceramic propant.

One of the most effective methods of increasing the productivity of obtaining hydrocarbon raw materials is hydraulic fracturing of a formation. The essence of this method is the production of a network of cracks in a low-permeability, poorly drained oil-gas formations by pumping a viscous fluid under high pressure into them. To keep the cracks open finely dispersed (0.4 – 2.0 m) spherical granules (propants) are added to the liquid pumped into the formation; penetrating into and filling a crack, propants create a strong disjoining framework with high oil and gas permeability. The working conditions determine the basic functional properties of propants, which must be capable of withstanding high formation pressures as well as the action of corrosive media (acidic gases, salt solutions) [1].

At the present time practically no ceramic propants are produced in Russia. For this reason, the enterprises in the domestic oil-gas producing industry must purchase such materials from foreign suppliers.

The existing propants are distinguished according to composition and a number of properties, including density and strength, and are subdivided into low-weight (bulk density no more than 1.54 $g/cm^3$) with medium strength and heavy-weight (bulk density more than 1.54 $g/cm^3$) with high strength. A ceramic propant with appropriate composition and properties is tailored to each oil (gas) deposit on the basis of the specific fracturing depth and width of the formation. Specifically, the advantages of propants with low density are seen in a medium with low and intermediate viscosity, more easily passed through the propant layer. Such propants are most effective in low and medium pressure wells and are ineffective in high-pressure wells. Consequently, the basic problem in developing a ceramic-propant technology is providing mutually competing properties of the granulated material, such as high strength with low bulk and apparent density.

Ordinarily, the chemical composition of the paste used to obtain propants includes aluminum and silicon oxides, whose content affects the qualitative characteristics of the granules. Aluminum oxide increases strength and silica affects the high-temperature elasticity of the material. Used together these materials make it possible to obtain spherical granules during subsequent sintering. These components are introduced into the mix with aluminum silicate initial material with $Al_2O_3$ content exceeding 28%[2] (clays, kaolins, bauxites, and their mixtures) and technogenic wastes (fly ash).

Large deposits of quite high-quality, refractory, clay raw material which holds promise for obtaining aluminum silicate ceramic propants are concentrated in the Ural – Siberian region. The products of dry enrichment of Russian kaolins from the Kampanovskoe deposit (Krasnoyarsk Krai) and the Zhuravlinyi Log deposit (Chelyabinsk Oblast) were tested in the present work. Foreign high-quality kaolin, widely used in various ceramic technologies, from the Prosyanovskoe deposit (Ukraine) was chosen for comparison.

A special feature of the raw kaolin from the Kampanovskoe deposit is the concentration of iron and tita-

[1] Tomsk Polytechnical Institute, Tomsk, Russia.

[2] Here and below — content by weight.



0361-7610/09/0910-0313 

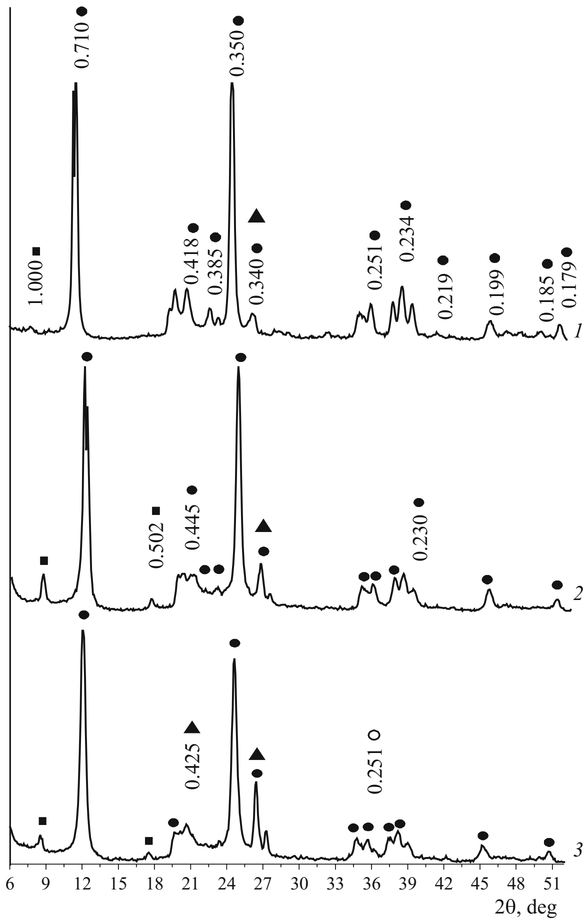


**Fig. 1.** X-ray diffraction patterns of the Prosyanovskoe (*1*), Zhuravlinyi Log (*2*), and Kampanovskoe (*3*) kaolins: ▲) quartz, ●) kaolinite, ■) illite, ○) hematite.

nium-containing impurities (up to 2.5%) predominately in finely dispersed fractions, which, independently of the enrichment method (dry or wet without chemical enrichment) and degree of enrichment, make it unpromising for use in manufacturing ceramic with white sherd. In addition, the presence of a high content (up to 25 – 30%) of finely dispersed quartz in enriched products increases the temperature of their complete sintering to above 1400°C [2].

The main rock-forming mineral component of Zhuravlinyi Log kaolin is kaolinite with halloysite. The quartz content in the raw kaolin from this deposit reaches 35 – 70%; the content of free quartz in the enriched kaolin does not exceed 3 – 5% [3].

On the basis of its mineral composition unenriched Prosyanovskoe kaolin is a mixture of kaolinite and quartz with a negligible amount of sericite, limonite, rutile, calcite, and zircon.

Commercially enriched kaolinite from the deposits indicated above was used as the initial aluminum silicate initial material.

According to the chemical composition and depending on the $Al_2O_3$ and $Fe_2O_3$ content in the calcined state, Prosyanovskoe and Zhuravlinyi Log kaolins belong to the group of basic clay materials ($Al_2O_3$ content above 40%) with a low content of coloring oxides, while the Kampanovskoe kaolin is distinguished by an elevated content of coloring and low-melting impurities (Table 1).

The x-ray data (Fig. 1) show that all three kaolins are a polymineral rock whose finely dispersed component (clay) is kaolinite, which is indicated by the strong, well-resolved, x-ray reflections with $d_\alpha/n = 0.714$, 0.357, 0.256 nm and others, together with a small amount of illitic hydromica ($d_\alpha/n = 1.040$, 0.448, 0.256 nm). The coarsely dispersed (nonclay) part of the kaolins consists primarily of quartz ($d_\alpha/n = 0.424$, 0.334, and 0.229 nm). Hematite ($d_\alpha/n = 0.269$ and 0.251 nm) was recorded in the Kampanovskoe kaolin.

It has now been proved that the properties of clays are determined not only by their mineral composition but also by the degree of crystallinity of the clay-forming minerals.

The degree of ordering of the clay minerals is determined qualitatively from the x-ray diffraction data. Specifically, the degree of perfection of the crystal lattice of kaolinite can be estimated by the Hinckley ordering index, which is determined from the degree of resolution of the x-ray triplet at angles from 18 to 24° (see Fig. 1). In the present case the ordering index (OI) of the main clay-forming mineral in Prosyanovskoe kaolin, equal to 1.2, attests to a high degree of ordering of the crystal lattice of kaolinite. For Zhuravlinyi Log kaolin the kaolinite is characterized by moderate ordering (OI = 0.9), Kampanovskoe kaolinite by low degree of crystallinity (OI = 0.6), as is confirmed by the electron microscopy data which make it possible to assess the shape and size of the kaolinite particles (Fig. 2).

In Prosyanovskoe kaolin the distinct outline of kaolinite platelets in the form of hexahedrons can be clearly seen in photomicrographs, while 0.5 – 2.0 μm particles of kaolinite from the Kampanovskoe deposit are characterized by more diffuse shapes with edges and corners broken off.

**TABLE 1.**

| Kaolin | Content, wt.% | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $TiO_2$ | $Fe_2O_3$ | CaO | MgO | $K_2O$ | $Na_2O$ | other |
| Prosyanovskoe | 46.42 | 37.71 | 0.64 | 0.67 | 0.45 | Traces | 0.65 | 0.22 | 13.04 |
| Zhuravlinyi Log | 47.06 | 36.29 | 0.21 | 1.01 | 0.80 | 0.20 | 0.73 | 0.29 | 13.01 |
| Kampanovskoe | 49.82 | 31.91 | 1.03 | 2.30 | 0.68 | 1.42 | 1.36 | 0.13 | 11.35 |

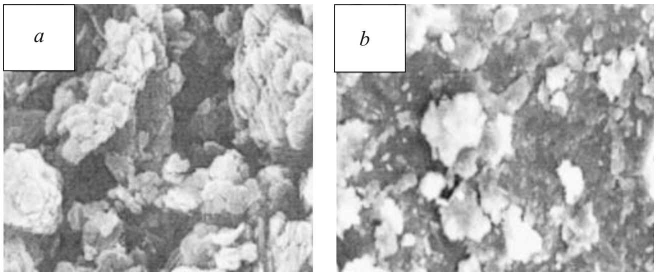


**Fig. 2.** Electron-microscopic photographs (× 5000) of Prosyanovskoe (*a*) and Kampanovskoe (*b*) kaolin.

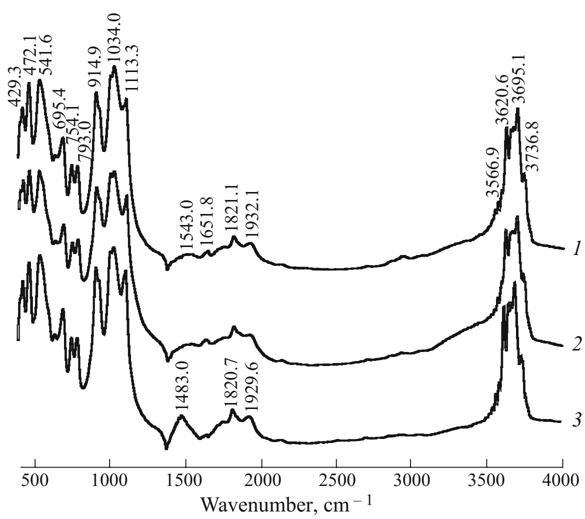


**Fig. 3.** IR absorption spectra of Zhuravlinyi Log (*1*), Kampanovskoe (*2*), and Prosyanovskoe (*3*) kaolins.

Together with x-ray diffraction, the diffuseness of the absorption bands at 1100 and 1035 $cm^{-1}$ in the IR spectra as well as the unresolvability of the two middle absorption bands of kaolinite in the region of the stretching and deformation vibrations of hydroxyl water at 3000 – 4000 $cm^{-1}$ attest to weak ordering of the kaolinite of Kampanovskoe kaolin, which is in contrast to Zhuravlinyi Log and especially Prosyanovskoe kaolinite (Fig. 3).

The degree of structural ordering of the main clay mineral affects the mullite formation process during sintering. Specifically, it is thought that the more ordered the structure, the easier it is for mullite to form, while more defects in the crystal structure of the clay material, the more strongly this process is impeded.

An investigation of the behavior of kaolins by means of differentially scanned calorimetry during heating (Fig. 4) showed that on the whole the DTA curves of all kaolins are characterized by the presence of a strong endothermal effect with a minimum at 522 – 532°C (depending on the form of the kaolin) due to losses of water of crystallization and amorphization of the mineral with some degree of structural ordering remaining in the kaolinite. The presence of a strong

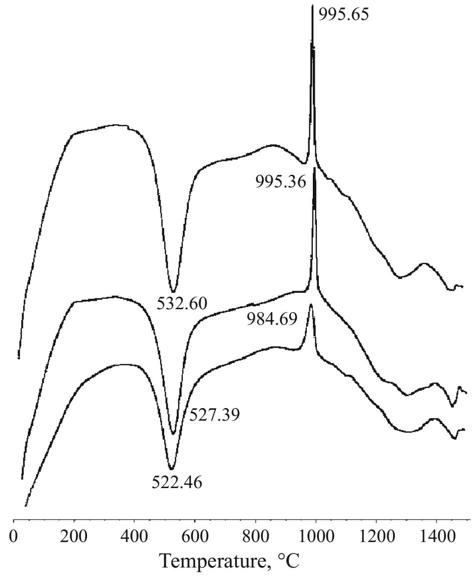


**Fig. 4.** DTA curves of Prosyanovskoe (*1*), Zhuravlinyi Log (*2*), and Kampanovskoe (*3*) kaolins.

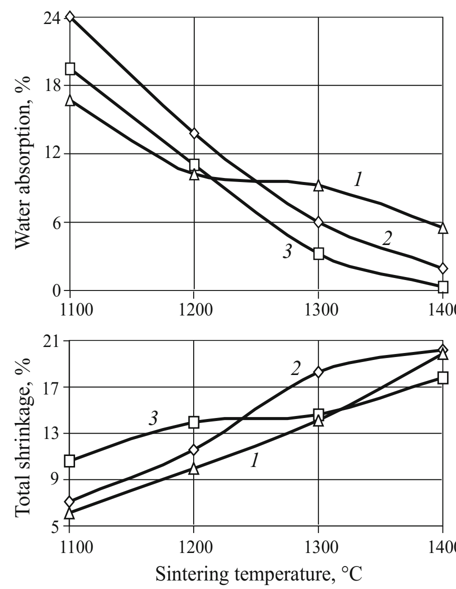


**Fig. 5.** Sintering curves of Prosyanovskoe (*1*), Zhuravlinyi Log (*2*), and Kampanovskoe (*3*) kaolins.

exothermal effect with a maximum in the temperature range 985 – 995°C is due to the crystallization of x-ray amorphous products of decomposition of kaolinite and the formation of mullite nuclei. Here, the 2 – 3 times stronger exoeffect in the DTA curves of Prosyanovskoe and Zhuravlinyi Log kaolins as compared with Kampanovskoe kaolin attests to more vigorous mullite synthesis in them.

An investigation of the behavior of enriched kaolins during sintering (Fig. 5) showed that because of the characteristics of the chemical – mineral composition Kampanovskoe kaolin sinters to water absorption no more than 2% already at

**TABLE 2.**

| Index | Kaolin | | |
|---|---|---|---|
| | Prosyanovskoe | Zhuravlinyi Log | Kampanovskoe |
| Phase composition of kaolin, wt.%: | | | |
| kaolinite | 95.5 | 91.9 | 80.8 |
| quartz | 2.0 | 4.8 | 12.2 |
| other minerals | 2.5 | 3.8 | 7.0 |
| Ordering index | 1.2 | 0.9 | 0.6 |
| Particle size, μm | 0.5 – 2.0 | 0.5 – 2.0 | 1.0 – 3.0 |
| Content of oxides in the heated state, wt.%, including: | | | |
| $Al_2O_3$ | 43.5 | 41.9 | 36.0 |
| $Fe_2O_3 + TiO_2$ | 1.5 | 1.4 | 3.8 |
| $K_2O + Na_2O$ | 1.0 | 1.2 | 1.7 |
| Complete sintering temperature, °C | 1450 | 1400 | 1350 |
| Compression strength in the sintered state, MPa | 111.3 | 102.0 | 82.5 |

temperature 1350°C, while the Zhuravlinyi Log and Prosyanovskoe kaolins sinter to this degree only at temperatures 1400 and 1450°C, respectively.

Comparing the data made it possible to obtain a quantitative estimate of the mineral composition of the initial clay material studied and to perform a comparative analysis of its basic physical – chemical and technological properties (Table 2).

The conventional technological scheme was used to test the experimental kaolins as a main material for aluminum silicate propants. This scheme included the following: briquetting of the kaolin, heat-treatment of the briquettes at 850°C to dehydrate the clay minerals, comminution of the product of heat treatment of kaolin to particle size less than 10 μm, granulation to bulk density 0.8 – 0.9 g/cm$^3$ (in the dry state) using a 0.3% solution of organic binder (carboxymethyl cellulose) in an amount ensuring moisture content of the material 16 – 26% as the wetting and plasticizing additive, intermediate sifting, sintering in the temperature range 1450 – 1500°C, and final sifting into commodity propant fractions.

The compression strength, bulk mass, sphericity, and roundness of the granules were determined for the granule fractions 16/20 (granule size 1.25 – 0.8 mm) and 20/40 (0.8 – 0.4 mm) obtained (Table 3).

In summary, all three kaolins manifest themselves differently in the technology of aluminum silicate propants. Specifically, when Prosyanovskoe kaolin is used the granules reach their required strength at sintering temperature 1450°C. When Zhuravlinyi Log kaolin is used the sintering temperature must be raised to 1500°C in order to obtain the same strength, while for Kampanovskoe kaolin this temperature is inadequate to obtain propants with the required strength.

To determine the reasons for the differences in the strength indicators of the granular material made from the experimental kaolins, the quantitative x-ray method was used to study phase formation in the experimental compositions.

The diffraction patterns of all products of sintering at temperatures that produce propants with the required strength (Prosyanovskoe kaolin at 1450°C, Zhuravlinyi Log and Kampanovskoe kaolins at 1500°C), are practically identical; they have the same set of x-ray reflections, the only difference being their intensity. Qualitatively, the presence of mullite, indicated by strong x-ray reflections for interplanar distances 0.540, 0.342, and 0.218 nm and quartz (0.425, 0.334, and 0.184 nm) as well as traces of cristobalite are noted in all compositions analyzed.

The degree to which mullite synthesis develops and different polymorphic forms of the silica component, as an impurity and a precipitate appearing as kaolinite undergoes thermal breakdown, were evaluated according to the change of the intensity of the x-ray reflection of mullite with interplanar distance 0.540 nm and quartz with 0.425 nm. The

**TABLE 3.**

| Kaolin | Fraction (size class) | Bulk density of dry granules, g/cm$^3$ | Sintering temperature, °C | Bulk density of the sintered granules, g/cm$^3$ | Fraction of fractured granules under pressure 52 MPa,* % | Sphericity and roundness of granules |
|---|---|---|---|---|---|---|
| Prosyanovskoe | 16/20 | 0.80 | 1450 | 1.55 | 16.0 | 0.8 – 0.9 |
| | 20/40 | 0.77 | 1450 | 1.52 | 5.5 | |
| Zhuravlinyi Log | 16/20 | 0.80 | 1450 | 1.38 | 39.9 | 0.8 – 0.9 |
| | 20/40 | 0.78 | 1450 | 1.41 | 25.4 | |
| | 16/20 | 0.80 | 1500 | 1.45 | 17.0 | |
| | 20/40 | 0.78 | 1500 | 1.45 | 6.3 | |
| Kampanovskoe | 20/40 | 0.82 | 1500 | 1.37 | 21.3 | 0.8 – 0.9 |

* GOST 51761–2005 requires that the fraction of fractured granules must not exceed 25% in the 16/20 fraction and 10% in the 20/40 fraction.

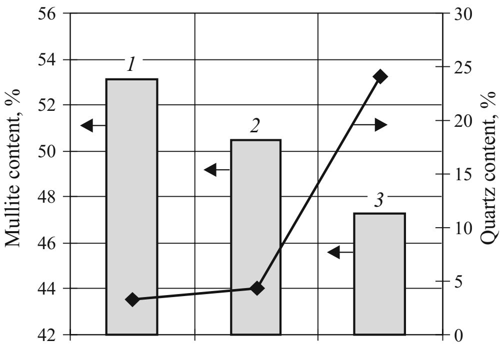


**Fig. 6.** Qualitative and quantitative compositions of the crystalline phase of propants based on Prosyanovskoe (*1*), Zhuravlinyi Log (*2*), and Kampanovskoe (*3*) kaolins with the optimal sintering temperature.

intensities of the corresponding reflections of fused mullite and vein quartz were used as standards (Fig. 6).

It was found that the main difference in the phase composition of the crystalline component of the product of sintering of Kampanovskoe kaolin at 1500°C, the highest temperature used but not giving a propant with the required strength, as compared with Prosyanovskoe and Zhuravlinyi Log kaolins, is the lower content of mullite and quite high content of residual quartz.

The higher mullite content is probably the main reason for the high strength of aluminum silicate propants based on Prosyanovskoe and Zhuravlinyi Log kaolins. For Kampanovskoe kaolin an additional softening factor is a high content of residual quartz with its polymorphic transformations.

In summary, when clay initial materials are used to fabricate ceramic propants with the required physical – chemical and strength properties the structure and phase formation processes must be steered in order to obtain the required crystalline phase (in this case mullite) with the highest possible yield.

The main criteria for suitability of clays and kaolins for obtaining aluminum silicate ceramic propants are the following: the kaolinite content in the clay raw material must be at least 90%; the content of free quartz must not exceed 5%; the content of alkaline oxides, which are responsible for the formation of the glass phase, must be 1.0 – 1.2%; and, the compression strength in the sintered state must be at least 100 MPa.

## REFERENCES

1. R. D. Kanevskaya, *Foreign and Domestic Experience in Using Hydrofracture of Formations* [in Russian], VNIIOÉNG, Moscow (1998).
2. T. V. Vakalova, V. I. Vereshchagin, E. Yu. Egorov, et al., "Refractory barrier materials for aluminum electrolyzers based on enriched Kampanovskoe kaolin," *Novye Ogenupory*, No. 11, 36 – 40 (2006).
3. A. S. Shamrikov, *Technology of Enrichment and Stabilization of the Ceramic Properties of Kaolins from the Zhyravlinyi Log Deposit, Author's Abstract of Candidate's Thesis* [in Russian], Tomsk (2002).